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Modelling Pesticide Run-Off to Surface Waters. Part I: Model Theory and Development

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Abstract: A conceptual model is presented to estimate the concentrations of pesticides appearing in surface waters following their application as part of agricultural production. The model has been formulated particularly to deal with soils that are prone to bypass flow and require artificial sub-surface drainage. Pesticide concentrations and loads can be calculated at field drainage outlets or for whole headwater catchments. The data required to run the model are generally readily available from published sources (within the UK) and these data have been detailed. The assumptions made in the model are stated and the limitations with respect to the general applicability of the model are discussed.

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Key words: mathematical model; pesticide; surface water; bypass flow; agriculture

1 INTRODUCTION

It has been reported that in water samples taken for pesticide analysis from 3500 sites within England and Wales during 1992 and 1993, 100 of the 120 pesticides targeted were detected.[1] Generally, detections were at small concentrations and in the cases of the 25 pesticides for which environmental quality standards have been set,[1] the latter were exceeded in less than 4% of samples. This same report goes on to highlight five herbicides (atrazine, diuron, bentazone, isoproturon and mecoprop) which regularly exceeded the EC Drinking Water Directive limit of 0·1 μg litre^{-1}. More importantly, these exceedances are likely to have arisen from diffuse sources following their approved use. Many plot, edge of field and small catchment experiments have been carried out in the UK[2–4] and in the USA[5] which support this assessment. However, it should be noted that in the case of atrazine (until 1992) and diuron, run-off may have resulted from approved non-agricultural use and that some run-off in agricultural areas may have resulted from chemical spills.[4] There is a need, however, for methods of estimating likely pesticide concentrations in surface waters resulting from the application of chemicals in the normal course of agricultural production.

Mathematical modelling is becoming a more widely used tool in estimating pesticide run-off. Perhaps the best-known model is GLEAMS (Ground water Loading Effects of Agricultural Systems[6]) which is intended to be used to compare the edge-of-field effects resulting from different agricultural management practices. While the pesticide concentrations predicted by GLEAMS are realistic, it is not a predictive model but a comparative tool. In common with many pesticide fate models, GLEAMS originally took no account of the possibility of bypass flow, lateral subsurface flow or flow through sub-surface drainage systems. All of these processes can contribute significantly to pesticide run-off.[3,4] However, recently GLEAMS has been modified to include crack flow through clay soils.[7] This has been achieved through considering the shrinkage characteristics of the soil, i.e. the interaction between water content and soil volume. If rainfall is sufficient to produce surface ponding and overland flow, crack flow

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may be initiated when cracks are predicted to be present. Water in the cracks moves straight through the soil profile until it reaches a model layer where no cracks are present. This modification is reported to give improved simulations in cracking clay soils.[7] The modified GLEAMS still does not consider lateral sub-surface flow or sub-surface drainage systems. Three recently developed models have demonstrated an ability to predict pesticide concentrations in soils where bypass flow, lateral sub-surface flow or flow through sub-surface drainage systems might be expected to occur; they are the models of Brooke, SoilFug and SWAT.[8–11]

The Brooke and SoilFug models are very similar, both being developments of the fugacity models of MacKay.[12,13] The models are essentially non-steady-state but equilibrium event models. They take into account the disappearance of the chemical according to different phenomena (degradation, volatilization, run-off) but then calculate the partition among the different phases of the soil using a level one fugacity model. SoilFug seeks to estimate the flow-weighted average concentration that occurs as the result of a whole rainfall event while the Brooke model looks at changes at a shorter (hourly) time step to predict variations through storm events. The flow mechanisms described above are not modelled explicitly in either model, but the hydrological response of the system is accounted for by using actual measured (or estimated) run-off amounts generated during each rainfall event. Indeed, the original model of Brooke assumed that all rainfall during an event entered the stream and this gave rise to poor predictions. A modified version allowing for only a percentage of rainfall to contribute to stream flow gave much better estimates, although the partially dissociated molecule, mecoprop, was still poorly simulated.[14]

The hydrological basis of SWAT is HOST (Hydrology of Soils Types[15]) which establishes a link between UK soil types and the amount of water moving rapidly to streams in response to rainfall. Attenuation factors, based on easily measurable physicochemical parameters, describe the decrease in concentrations of pesticide between field application and loss in run-off water. The objective is to predict maximum concentrations in transient peaks of pesticide reaching surface waters as a result of individual rainfall events.

A more physically based, deterministic approach to modelling solute transport through macroporous soils is taken by two other leaching models, CRACK and MACRO.[16,17] Both of these models estimate vertical leaching, but also estimate potential run-off to surface waters at the field scale through simulation of surface run-off and export through sub-surface drainage systems.[18] While both models explicitly model macropores and allow for exchange of water between macropores and the soil matrix, CRACK assumes that flow occurs mainly in the macropores and that matrix flow is insignificant, while MACRO allows flow in both domains. A full comparison of the two models is given elsewhere.[19]

The model presented here seeks to include explicitly, at the small catchment scale, the hydrological pathways that represent bypass flow, sub-surface lateral flow and flow to sub-surface drains. These are the dominant processes in many UK agricultural soils. The flow paths for water are treated as the main control on the arrival of a pesticide at surface waters, while the physicochemical properties of sorption and half-life exert control over the amount of pesticide available for transport. The model is based on a conceptualization of a drained soil and simulates flow rates and pesticide concentrations over the main drainage season. The objective of this modelling approach is to be able to simulate changes, at an hourly time step, in pesticide concentrations in waters receiving run-off through the course of individual rainfall events. This allows both the peak and duration of events to be estimated, thus allowing a better estimate of any potential environmental impacts.

2 MODEL STRUCTURE

The model structure presented here was derived from detailed measurements of the soil water movement and distribution in a drained field over successive winters.[20,21] Broadly, the study showed that an under-drained field consists of two types of soil profile which are characterized by the rate at which they allow downward water movement. The bulk of the soil in the inter-drain position has a very small hydraulic conductivity which approaches zero when the soil is saturated; downward water movement through the soil matrix is therefore very slow. The soil above the drains has a much greater hydraulic conductivity and thus water movement through the soil matrix in this part of the field is much quicker. Thus, once the soil below the drains is saturated and the drains begin to flow, the hydrological response of the drain is controlled by the soil immediately above and adjacent to the drains.

A diagrammatic representation of the model is shown in Fig. 1. The model considers the top 2 m of the soil profile, which is divided into three layers above the level of the drains and one below. Above the drain the layers are subdivided into two, representing the fast and slow parts of the soil profile described above. Agricultural fields are generally sloping, and, in this conceptualization, the drain zone is considered to be down slope of the inter-drain zone. The consequent possible directions of water movement are shown by the arrows in Fig. 1, where dotted arrows indicate the possibility of water moving directly to lower layers (via macropores) without interacting with intervening layers. Thus, the model allows explicitly for bypass flow to occur within the soil profile.

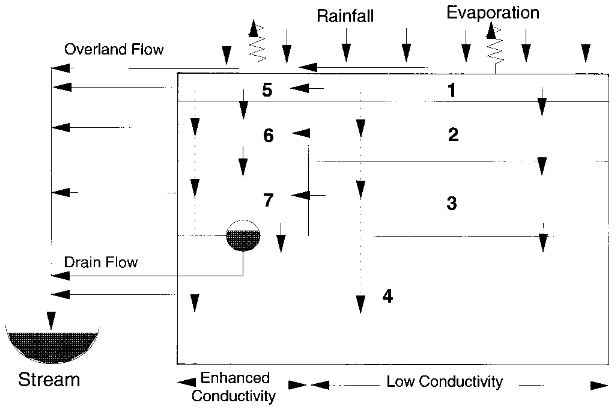

Fig. 1. Representation of the conceptual pesticide model showing the flow pathways between the soil boxes. Dotted lines indicate the possibility of bypass flow.

The transport of pesticide in the system is assumed to be associated with the water movement, with pesticide being re-partitioned between the soil and water phases at the end of each time step (1 h). The model keeps account of the amounts of water and the dissolved and adsorbed pesticide in each box and calculates changes to these, depending on a mass balance of inputs, outputs and internal sources and sinks.

2.1 Water movement

To explain the details of water and pesticide movement it is best to consider a single box from the model (Fig. 2). Let the subscript i be used to refer to one of the seven boxes in Fig. 1 above. The change in soil water content of box i, S_i is given by

$$\frac{dS_i}{dt} = q_{i-1} - qbp_i + d_u - q_i - dl_i + qbm_{i-1} \qquad (1)$$

where q_i is the flow per unit area (mm) from box i; qbp_i is the flow from box $i-1$ that bypasses box i in cracks or macropores; d_u is the flow per unit area (mm) from an up-slope box, dl_i is the flow to a down-slope box or stream and qbm_{i-1} is the flow that was in bypass routes in box $i-1$ that return to the soil matrix in box i; t is time (hours). For the top two model boxes, 1 and 5, the inflow to the box is rainfall minus evaporation. Flow may only occur from box i, either vertically (q_i) or laterally (dl_i) when $S_i > SFC_i$, where SFC_i is the field capacity of box i. Flow from box i depends on the water content of box 1 and is given by

$$q_i = kv_i(S_i - SFC_i)(1 - \tan(\alpha)) \qquad (2)$$

where kv_i (h^{-1}) is a measure of the vertical conductivity of box i, and α is the average slope of the field (degrees). Similarly the down-slope drainage dl_i is given by

$$dl_i = kh_i(S_i - SFC_i)\tan(\alpha) \qquad (3)$$

where kh_i is a measure of the horizontal conductivity of box i. Both the horizontal and vertical conductivities are assumed to vary with water content in a similar manner,

$$kv_i = (S_i/SMAX_i)^3 SATkv_i \qquad (4)$$

where $SATkv_i$ is the horizontal conductivity when the soil in box i is saturated. It is possible to set a minimum value for the conductivity which is used until such a time as it is exceeded by the value calculated by eqn (4).

A fraction of water may bypass a given layer through macropores and cracks. Some clay soils swell when wet and shrink on drying, resulting in differing macropore densities through the season. Under rainfall conditions that result in ponding and overland flow, summer cracks can result in increased bypass flow to depth. The model presented here is only for use in the drainage period when soil moisture levels will be sufficiently high to reduce cracking to a minimum and large macropores will be limited to those that occur due to old root channels and earthworm burrows. Therefore,

$$qbp_i = CF_i q_i \qquad (5)$$

where CF_i is the macropore flow fraction in the ith box. The continuity of cracks through layers is given by the ratio, CF_i/CF_{i-1} to a maximum of unity. Thus, once in a crack, water is assumed to remain there until the crack ends. Hence,

$$qbm_i = \left(1 - \frac{CF_i}{CF_{i-1}}\right) qbp_{i-1} \qquad (6)$$

In general the number of bypass flow routes will decrease with depth, thus some proportion of the cracks will end in various of the model boxes. As bypass flow routes terminate, the water they are carrying is assumed to remix with the water in the soil matrix of the box in which they terminate.

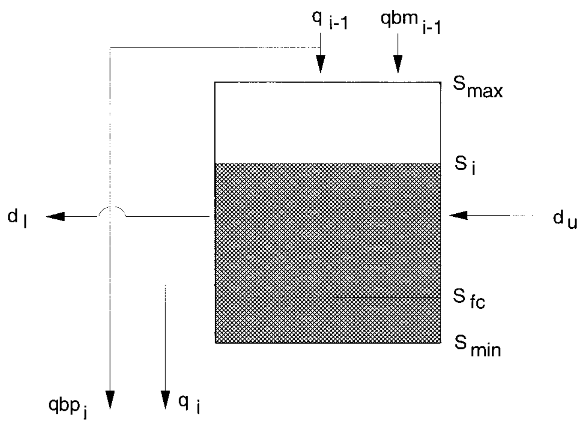

Fig. 2. Flow paths contributing to the mass balance around a soil box.

Water may only enter a box if it is not saturated (ie $S_i < SMAX_i$); $SMAX_i$ is given by;

$$SMAX_i = \phi_i V_i \quad (7)$$

where ϕ_i and V_i are respectively the porosity and volume per unit area (mm) of box i. This is not the case for water draining from boxes 3 and 7 into box 4 when it is saturated. In this case water will displace that already in box 4 into the drainage system and thus generate drainflow.

2.2 Pesticide movement

Pesticide is added to the model by assuming that the amount applied is well mixed into the top layer of the model (boxes 1 and 5, Fig. 1) and partitioned between the soil and the soil water following a reversible instantaneous linear sorption isotherm

$$PS_i = PW_i^* k_{di} \quad (8)$$

and

$$k_{di} = k_{oc} OC_i \quad (9)$$

where PS_i is the pesticide concentration in the soil phase (μg kg^{-1}), PW_i^* is the concentration of the pesticide in the dissolved phase (μg litre^{-1}), k_{di} is the partition coefficient (litre kg^{-1}) and k_{OC} is the partition coefficient (litre kg^{-1}) normalized for fractional content of organic carbon, OC_i.

Assuming that each of the boxes in Fig. 1 is well mixed, then the rate of change of mass of dissolved pesticide in the ith box, ($S_i PW_i$) is given by

$$\frac{dS_i PW_i}{dt} = (q_{i-1} - qbp_i)PW_{i-1} + du_i PW_u - (q_i + dl_i)PW_i + qbm_{i-1} PW_{bm} - R_d S_i PW_i \quad (10)$$

where PW_i is the dissolved pesticide concentration per unit area of the ith box, PW_u is the pesticide concentration of water draining from an up-slope box, PW_{bm} is the concentration of pesticide in the bypass flow and R_d is the first-order rate coefficient describing degradation of the pesticide. Water moving through bypass routes is assumed to have the same concentration as the soil water in the box with which it was last in contact. The rate of change of mass of pesticide adsorbed onto the soil is given by;

$$\frac{dPS_i}{dt} = -R_d PS_i \quad (11)$$

where PS_i is the soil-adsorbed pesticide concentration per unit area in the ith box (μg kg^{-1}). New concentrations of the pesticide are thus calculated for the end of each model time step. These concentrations may not, however, be in equilibrium. Therefore, the total pesticide in each of the boxes is calculated from the dissolved and solid-phase concentrations and then partitioned using eqn (8). These new equilibrium values are then taken to be the starting points for the next model time step.

2.3 Drain flow

The model only allows drain flow when the deep soil box, (box 4, Fig. 1) is at saturation. When this occurs, drain flow is the sum of the vertically draining water from boxes 3 and 7 plus any water from rainfall and boxes 5 and 6 moving via bypass routes that are connected to the drain. Thus, for any time step in which drain flow occurs,

$$D_f = (q_7 + qbp_7 + qbp_6 + qbp_5)f + q_3(1 - f) \quad (12)$$

where D_f is the drain flow (mm h^{-1}) and f is the ratio of the enhanced conductivity area to the total area of a representative drainage element (see Fig. 1). Water moving from boxes 3 and 7 is assumed to produce drain flow by displacement of water from box 4, while water in bypass routes is directly intercepted by the drain. If the amount of water arriving at box 4 during a time step is in excess of the saturation deficit in that box, then drain flow will occur but will be reduced by the amount necessary to satisfy the deficit. The pesticide concentration of the drain flow, D_p, is given by a mass balance of the contributions from the various flow paths. Note that it is possible for part of the rainfall to bypass the top box and proceed directly to the next layer. In practice however, the thin top layer is used in the model as a mixing zone for incoming rainfall and applied pesticide and therefore is assigned few macropores. This is very likely to be the case after the cultivation of a new seed bed. Water with a potentially large concentration of pesticide may then bypass lower boxes to reach the drain directly. Water behaving in this manner will, in the model, have a concentration equal to that of any overland flow that might be generated (see below).

$$D_p = \frac{((q_7 PW_4 + qbp_7 PW_6 + qbp_6 PW_5 + qbp_5 PW_r)f + q_3 PW_4(1 - f))}{D_f} \quad (13)$$

where PW_r is the concentration of the pesticide in the rainfall (usually zero).

2.4 Stream flow

Stream flow is the sum of the lateral drainage from boxes 5–7, drain flow and a base flow term, B_f

(mm h^{-1}). B_f is the value of the minimum stream flow which occurs when all the soil boxes are dry. The model assumes the dynamic response of the catchment is controlled by the upper soil layers and there is little or no connection with the ground water. However many streams from surface-water-dominated catchments are perennial, being sustained by springs resulting from recharge external to the surface water catchment, hence the term B_f. The stream flow (mm h^{-1}) during a model time step is given by

$$S_f = D_f + (dl_5 + dl_6 + dl_7 + dl_r)f + dl_4 + B_f \quad (14)$$

Again the concentration of pesticide in the stream, S_p, is calculated from a mass balance of the contributions from all the flow paths, thus,

$$S_p = \frac{D_f D_p + (dl_5 PW_5 + dl_6 PW_6 + dl_7 PW_7 + dl_r PW_5)f + dl_4 PW_4 + B_f B_p}{S_f} \quad (15)$$

where dl_r is the water entering the stream as overland flow and B_p is the pesticide concentration of the stream base flow (often zero). Overland flow is generated when the water content of either box 1 or box 5 is calculated to be in excess of the saturated value. This condition is checked at each hourly time step and the amount of overland flow in that hour is set to the difference between the saturated and calculated values. The water content of the box is reset to the saturated value. The water content of box 1 or box 5 will be in excess of the saturated value if, in any one time step, the amount of rainfall less the evaporation exceeds the amount of water draining from the box plus any unfilled porosity below the saturated value. Water flowing overland from box 1 will infiltrate into box 5 if this box is not saturated and overland flow from box 5 will enter the stream directly. The concentration of pesticide in the overland flow is assumed to be equal to the concentration of the box from which it was generated.

3 MODEL ASSUMPTIONS AND LIMITATIONS

All models are based on a number of assumptions which will have a bearing on the circumstances in which the model can be applied. The assumptions implied in this conceptualization are considered below. The limitations arising from these are then discussed.

(i) The model has been developed using data from only one field study and only this data set has been used to test the performance of the model.[22] There is always a concern in such cases that the conceptualization of the model may be specific to a particular site. Furthermore, the data required to run the model may not be generally available and thus its use becomes restricted. This last point is considered below.

(ii) The model assumes that the soil profile can be modelled as a series of linked, well-mixed boxes. In reality the concentration through the length of the soil profile represented by a box will vary. For this reason the approach suggested here will not predict leaching depths for pesticides accurately. However, the approach should give a good estimation of the pesticide that is available to be removed from the profile at any given time after application.

(iii) The model is a lumped model, i.e. parameters are given a single value to represent an entire compartment. There is no spatial variability in the rate of movement of water and pesticide to the catchment outlet, other than that allowed by the separation of the elements above and between the drains. Thus the size of catchment that can be modelled using this approach is limited.

(iv) The model assumes that the movement of water through the soil profile is predominantly downward and should only be run for single drainage seasons.

(v) Implied in the model conceptualization is the assumption that all, or at least an extensive proportion, of the catchment is artificially drained. This further implies that the model would not be suitable to be used in situations where overland flow is the predominant source of entry into stream flow.

(vi) The conceptualization is based around a cracking soil with macropores.

(vii) The model assumes that the pesticide sorbs reversibly onto the solid phase and that changes in pesticide concentrations can be re-equilibrated at the end of each model time step.

(viii) The degradation of the pesticide, by whatever means, is assumed to be adequately described using a first-order decay rate. It is further assumed that degradation rates are constant through the drainage season.

(ix) The crop density is assumed to be sufficiently low not to intercept a significant proportion of either rainfall or the applied pesticide.

(x) The hydrological year starts on 1 September, and it is assumed that soil water stores are at their minimum at this time.

Of all the model limitations outlined above, the first three are the most important; (ii) and (iii) are basic

assumptions in the conceptualization of the model and (i) emphasizes the limited testing to which the model has been subjected. The conceptualization can be considered to be independent of location and will not affect the general applicability of the model, other than in the size of catchment that can be modelled as a single entity.

Assumptions (vii) and (viii) are commonly used in pesticide modelling and reflect the general availability of data to describe these processes. Assumption (iv) is again a critical restraint on the use of the model. The model allows only for the downward movement of water and can thus be applied only to a soil profile which is draining. Therefore, any redistribution of pesticide that might occur due to the reversal of the water potentials caused by high evaporation cannot be modelled. In the UK, this means that the model should only be applied from late autumn to early spring. However, this time frame covers the hydrological conditions most likely to lead to pesticide run-off and should not prove to be a practical limitation. The starting date for the model is fixed assuming that 1 September is the start of the hydrological year; in most years (and most locations within the UK) this assumption will hold. This assumption is made only in order to give a fixed starting point for the amounts of water held in the model boxes. If the water contents of the seven boxes were known at a given time in the year, these could be input as the initial conditions in the model and the simulation carried out as normal.

Only assumptions (v) and (vi) make specific demands on the soil type and drainage within a catchment on which the model is to be run. The model contains parameters that may be used to alter the macroporosity of the soil and the extent of the drainage network so as to minimize the limitations of these assumptions. However, if the fraction of the catchment drained and the macroporosity were to be set to zero, then care should be taken to ensure that the model produces sensible results. One approach would be to compare the hydrographs produced by the model with observed data (these data are generally more readily available than pesticide data).

4 DATA REQUIREMENTS

The data required to run the model are summarized in Table 1. The majority of these data are relatively easy to find, particularly within the UK. Soils data, for example, are available from a personal computer based system called SEISMIC at a resolution of 5 km^2 and

TABLE 1
Data Required to Run the Pesticide Run-Off Model

Data type	*Description*	*Extent*
Catchment	Catchment area (ha)	
	Area drained (ha)	
	Slope (degrees)	Catchment average to surface water
	Base flow (mm h^{-1})	Single value for the stream
Meteorological	Rainfall (ha)	Hourly time series
	Potential Evaporation (mm)	As above
Soil physical properties	Depth of boxes representing soil profile (mm)	For each soil layer
	Minimum water content (mm)	For each of the seven model boxes
	Field Capacity (mm)	As above
	Porosity (%)	As above
	Bulk Density (kg litre^{-1})	As above
	Organic carbon content (%)	As above
	Macropore volume (%)	As above
Soil hydraulic properties	Vertical flow rate parameter (h^{-1})	As above
	Horizontal flow rate parameter (h^{-1})	As above
	Fraction of hydrological unit with enhanced conductivity	Single value for the catchment
Pesticide application data	Date	For each application
	Rate (kg AI ha^{-1})	As above
	Area treated (ha)	As above
Pesticide properties	k_d or k_{oc} (litre kg^{-1})	For each pesticide
	Half-life (days)	As above

the data required for this model could be found from within this system.[23] The exceptions to this are the parameters describing the abundance of macropores in the model boxes. A measure of this value, however, might be found from study of the low tension end of the water release curve. Water tensions can be equated to approximate pore sizes that will be holding water at that tension; macropores hold water only at low tensions.[24] Choosing a suitably low tension to represent macropores of an appropriate size will enable the fraction of the porosity associated with macropores to be calculated from the area of the water release curve with tensions lower than the selected value. Pesticide physicochemical properties are readily available from a number of reference works.[22,26] It is noted, however, that caution should be exercised in using data derived from field experiments conducted under conditions that differ from the intended model application. It is invariably best to obtain field measurements of degradation rates from the catchment to be modelled.

Rainfall data and estimates of potential evaporation should be available from local meteorological stations. These data are the driving variables for the model and the frequency of their measurement will control the model time step. Hourly data for rainfall and daily values for evaporation are the shortest time step at which these data are readily available, hence the use of an hourly time step in this model. In theory other model time steps could be used but this has not been tested. Often, however, model runs are used to estimate the likelihood of leaching at specific sites. In these cases synthetic time series of data can be used that reflect the local meterorological conditions. Data about the catchment size and pesticide applications should be known for the particular model application.

The most difficult parameters to specify are those that control the horizontal and vertical movement between boxes. Because the model approach described here is conceptual in design, it is not possible to take the values of these parameters directly from measurable soil hydraulic parameters. However, the relative magnitudes of these parameters should be related to the soil hydraulic conductivity values and this will give some limits in defining these values.

5 CONCLUSIONS

This paper has represented a conceptual model of pesticide run-off to surface waters that may help address the need for improved tools to aid in the assessment of the risk posed by the approved use of pesticides in agriculture. The aim of the model is to estimate the peak concentration and duration of pesticide losses to streams during rainfall events following application to land. The model has undergone only limited testing on one catchment and as this catchment also contributed to the conceptualization of the model caution would be needed in applying it elsewhere. The majority of the model parameters can be estimated from readily available data and, within the limitations discussed, the possibility exists that the mode could be applied more generally.

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REFERENCES

1. National Rivers Authority, Pesticides in the Aquatic Environment. *Water Quality Series No. 26*, HMSO, London, UK, 1995.
2. Williams, R. J., Brooke, D. N., Matthiessen, P., Mills, M., Turnbull, A. & Harrison R. M., Pesticide transport to surface waters within an agricultural catchment. *J. IWEM*, **9** (1995) 72–81.
3. Johnson, A. C., Haria, A. H., Bhardwaj, C. L., Volkner, C. & Walker A., Water movement and isoproturon behaviour in a drained heavy clay soil: 2 Persistence and Transport. *J. Hydrol.*, **163** (1994) 217–31.
4. Harris, G. L., Bailey, S. W. & Mason, D. J., The determination of pesticide losses to water courses in an agricultural clay catchment with variable drainage and land management. In *Proc. Brighton Crop Prot. Conf.—Weeds, 1991*. British Crop Protection Council, Farnham, Surrey, **3** (1991) 1271–8.
5. Burgoa, B. & Wauchope, R. D., Pesticides in run-off and surface waters. In *Environmental Behaviour of Agrochemicals*, ed. T. R. Roberts and P. C. Kearney. John Wiley & Sons, Chichester, UK, 1995, pp. 221–55.
6. Leonard, R. A., GLEAMS: Groundwater Loading Effects of Agricultural Systems. *Trans. ASAE*, **30** (1987) 1403–18.
7. Morari, F. & Knisel, W. G., Modification of the GLEAMS Model for Crack Flow. *Trans. ASAE*, **40** (1997) 1337–48.
8. Brooke, D. & Matthiessen, P., Development and validation of a modified fugacity model of pesticide leaching from farmland. *Pestic. Sci.*, **31** (1991) 349–61.
9. Williams, R. J., Brooke, D. N., Matthiessen, P., Mills, M., Turnbull, A. & Harrison, R. M., Pesticide transport to surface waters within an agricultural catchment. *J. IWEM*, **9** (1995) 72–81.
10. DiGaurdo, A., Williams, R. J., Matthiessen, P., Brooke, D. N. & Calamari, D., Simulation of pesticide run-off at Rosemaund Farm (UK) using the SoilFug model. *Environ. Sci. Pollut. Res.*, **1** (1994) 151–60.
11. Brown, C. D. & Hollis, J. M., SWAT—A semi-empirical model to predict concentrations of pesticides entering surface water from agricultural land. *Pestic Sci.*, **47** (1996) 41–50.
12. Mackay, D. & Paterson, S., Calculating fugacity. *Environ. Sci. Tech.*, **15** (1981) 1006–14.
13. Mackay, D., *Multimedia Environmental Models. The Fugacity Approach.* Lewis Publishers Inc., Michigan, USA, 1991.
14. Williams, R. J., Brooke, D. N., Glendinning, P. J., Matthiessen, P., Mills, M. J. & Turnbull, A., Measurement and

modelling of pesticide residues at Rosemaund Farm. In *Proc. Brighton Crop Prot. Conf.—Weeds, 1991*. British Crop Protection Council, Farnham, Surrey, **2** (1991) 507–14.
15. Boorman, D. B., Hollis, J. M. & Lilly, A., Hydrology of soil types: a hydrologically-based classification of the soils of the UK. *Institute of Hydrology Report No. 126*, Wallingford, UK, 1995.
16. Jarvis, N. J. & Leeds-Harrison, P. B., Modelling water movement in drained clay soil. I. Description of the model, sample output and sensitivity analysis. *J. Soil Sci.*, **38** (1987) 487–98.
17. Jarvis, N. J., CRACK: a model of water and solute movement in cracking clay soils. *Swedish Univ. of Agric. Sci., Report No. 159*, Uppsala, Sweden, 1989.
18. Jarvis, N. J., The MACRO model (Version 3.1). Technical description and sample simulations. *Department of Soil Sciences—Reports and Dissertations*, **19** (1994) 51 pp., Swedish Univ. of Agric. Sci., Uppsala, Sweden.
19. Armstrong, A. C., Addiscott, T. M. & Leeds-Harrison, P. B., Methods for modelling solute movement in structured soils. In *Solute Modelling in Catchment Systems*, ed. S. T. Trudgill. John Wiley & Sons Ltd, Chichester, UK, 1995, pp 135–61.
20. Williams, R. J., Total impact assessment of pollution in river basins: Pesticide impact modelling. *National Rivers Authority*, *R&D Note 404*, Foundation for Water Research, Marlow, UK, 1995.
21. Williams, R. J., Brooke, D. N., Clare, R. W., Matthiessen, P. & Mitchell, R. D. J., Rosemaund pesticide transport study 1987–1993. *Institute of Hydrology Report No 129*, Wallingford, UK, 1996.
22. Williams, R. J., Modelling pesticide run-off to surface waters, Part II: Model application, *Pestic. Sci.*, .
23. Hollis, J. M., Hallet, S. H. & Keay, C. A., The development and application of an integrated database for modelling the environmental fate of herbicides. In *Proc. Brighton Crop Prot. Conf.—Weeds, 1993*. British Crop Protection Council, Farnham, Surrey, **3** (1993) 1355–64.
24. Koorevaar, P., Menelik, G. & Dirksen, C., *Developments in Soil Science* **13:** *Elements of Soil Physics*. Elsevier, Amsterdam, The Netherlands, 1983.
25. Wauchope, R. D., Buttler, T. M., Hornsby, A. G., Augustin Beckers, P. W. M. & Burt, J. P., The SCS/ARS/CES pesticide properties database for environmental decision making. *Rev. Environ. Contam. Toxicol.*, **123** (1992) 1–164.
26. Tomlin, C., (Ed.) *The Pesticide Manual*, 10th edn. British Crop Protection Council, Farnham, UK, 1994.